# Field and Frequency Dependence of the Dielectric Response of Zr-rich PZT at the FRL-FRH and FRH-PC Phase Transitions

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*Published in:*
Journal of the Korean Physical Society



*Publication date:*
1998

Journal of the Korean Physical Society, Vol. 32, Feburary 1998, pp. S273∼S276

# Field and Frequency Dependence of the Dielectric Response of Zr-rich PZT at the $F_{RL}$-$F_{RH}$ and $F_{RH}$-$P_C$ Phase Transitions

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Dielectric permittivity and dielectric losses have been investigated in Zr rich $Pb_{1-y/2}(Zr_{1-x}Ti_x)_{1-y}\ Nb_yO_3$ (x = 0.035 ± 0.005, y = 0.039 ± 0.013) at the $F_{RL}$ - $F_{RH}$ and the $F_{RH}$ - $P_C$ phase transitions for three frequencies (1, 100, 500 kHz) and three a.c. field amplitudes (7.3, 21.8, 65.5 V/cm). The frequencies investigated are sufficient to show the presence of three different phenomena: ionic conductivity, domain wall dielectric relaxation, not well described with these data, and piezoelectric resonances. The dependence of the dielectric response with temperature and field near both transition are reported in the vicinity of both phase transitions.

## I. INTRODUCTION

PZT is known to have application in pyroelectric detectors, piezoelectric transducers, etc. The dielectric behavior of the high temperature ferroelectric-rhombohedral ($F_{RH}$) to paraelectric-cubic ($P_C$) phase transition has been recently studied as a function of titanium and niobium contents [1,2]. The presence of another phase transition from a $F_{RL}$(ferroelectric rhombohedral - low temperature) to a $F_{RH}$(ferroelectric rhombohedral - high temperature) at a temperature $T_{LH}$ close to room temperature for Zr-rich PZT, makes this material interesting among other things for energy conversion applications [3].

## II. EXPERIMENTAL

In this work we present results of dielectric measurements for three frequencies (1, 100 and 500 kHz) and three a.c. field amplitudes (7.3, 21.8 and 65.5 V/cm) as a function of the temperature.

We have used ceramic PZT samples with composition $x = 0.035 \pm 0.005$ and $y = 0.039 \pm 0.013$. They were prepared and sintered at 1340 °C for 1.5 h at the laboratories of the Shanghai Institute of Ceramics, CAS. The samples were disks with 1.1 mm in thickness and 1.5 cm in diameter with silver paint electrodes.

We collected data for all nine compositions mentioned but we show only the data for one specific composition, $x = 0.035$, $y = 0.039$. The remaining ones show similar behavior and the observed composition dependence at 1 kHz is analyzed elsewhere [2].

The dielectric constant and losses factor of the sample was measured for both heating and cooling runs at 20 °C/h by means of an automatic HP-LCR Meter (model 4284A) and the temperature was determined using a thermocouple connected to a Keithley 196 DMM digital multimeter.

## III. RESULTS AND DISCUSSION

For low Ti concentration PZT presents clearly a first order phase transition between a ferroelectric-rhombohedral of high temperature phase ($F_{RH}$) and the paraelectric cubic phase ($P_C$) at $T=T_{FP}$ ,as shown in Fig. 1 and Fig. 2. Figure 1 shows the results for the inverse of the dielectric constant, $\epsilon^{-1}$, and losses factor, D, *vs.* T for three different frequencies and $E_o$ = 7.3 V/cm, for the a.c. field amplitude, through $T_{FP}$. In Fig. 1.(a) a small difference between the curves for 1 kHz and 100 kHz appears near the phase transition, but for 500 kHz, $\epsilon^{-1}$ the behavior shown is somewhat different. It shows the influence of the closest piezoelectric resonance in the thickness mode (about 2 MHz). The effect is amplified near the phase transition because of the singular behavior of the piezoelectric constant as discussed below.

At the lowest frequency (1 kHz) the dielectric losses clearly grow with temperature in the range $T > T_{FP}$ (see Fig. 1). This phenomenon does not appears at 100 kHz. Ionic conductivity contributes substantially to increase the dielectric losses at high temperatures, but this effect is strongly weakened at higher frequency. Because we are using frequencies far below the infrared, the electronic contribution to the conductivity can be taken as independent of frequency [4]. Then, the ionic contribution becomes predominant at sufficiently high temperature and low enough frequency.

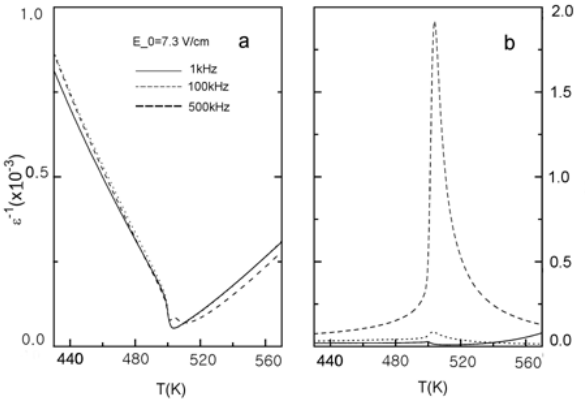


Fig. 1. Inverse of dielectric constant for three different frequencies and $E_o$=7.3 V/cm field amplitude for Zr rich PZT.

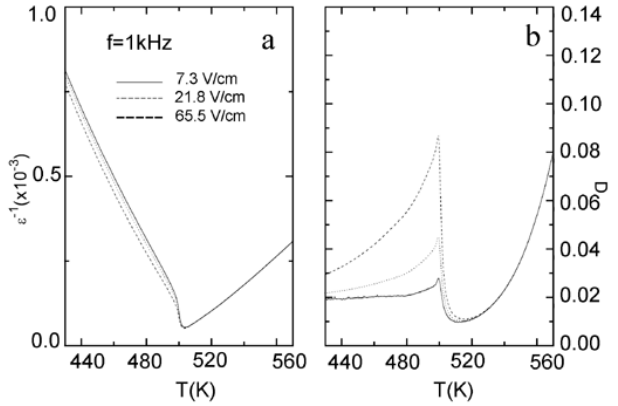


Fig. 3. Inverse of dielectric constant for the lowest frequency used in this work and three different field amplitudes.

The imaginary part of the dielectric permittivity is affected by the ionic conductivity and depends on frequency $\omega$ and temperature T in the following way:

$$\epsilon''(\omega,T) = \epsilon''_{\rm o}(\omega,T) + \frac{4\pi}{\omega}\sigma'(\omega,T), \quad ({\rm esu-cgs\quad units}) \tag{1}$$

where $\epsilon''_{\rm o}$ is the imaginary part of the dielectric constant without conductivity, and $\sigma'$ is the real part of the conductivity. As mentioned above, the conductivity has two contributions: electronic, $\sigma_o$, and ionic $\sigma_{at}$. This last one has a marked effect above certain temperature, and tends to disappear when the frequency is increased (see Fig. 1(b)). The ionic conductivity can be written as

$$\sigma_{\rm at} = \frac{\sigma_{\rm at}(0)}{1+\omega^2\tau_{\rm at}^2} \quad , \quad \sigma_{\rm at}(0) = C(T)e^{-\Delta U/k_B T} \tag{2}$$

where $\tau_{\rm at}$ is the ionic relaxation time and $\sigma_{\rm at}(0)$ is the dc ionic conductivity. It involves heavy ions in the vibrating process, in such a way that it is strongly damped at relatively low frequencies ($\sim$ 100 kHz). Then, the effect of the ionic conductivity appears at high temperature ($\sim$ 520 K) but only in the lowest frequency investigated.

In the literature, domain wall relaxation has been reported at about 100 kHz for other ferroelectrics [5]. However, other effects like ionic conductivity are important in our samples in this range of frequencies, and, probably, domain wall relaxation, which is expected to become important at $T$ close to $T_{\rm C}$ is masked by these other effects. In any case, for a detailed characterization it is necessary to have data at closely spaced frequencies in this range. For completeness we give the Debye like equation applicable for domain wall relaxation,

$$\epsilon'(\omega) = \epsilon_{\rm wo} + \frac{(\epsilon_{\rm ws}-\epsilon_{\rm wo})}{1+\omega^2\tau_{\rm w}^2} \tag{3}$$

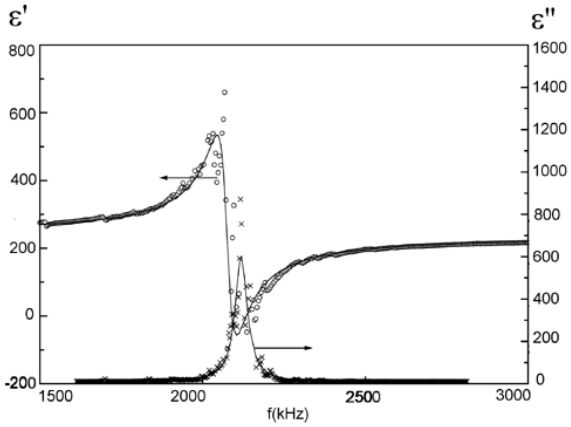


Fig. 2. Real ($\epsilon'$)(open circles) and imaginary ($\epsilon''$)(crosses) part of the dielectric constant at room temperature versus frequency in the thickness mode piezoelectric resonance (fundamental frequency) for Zr rich PZT.

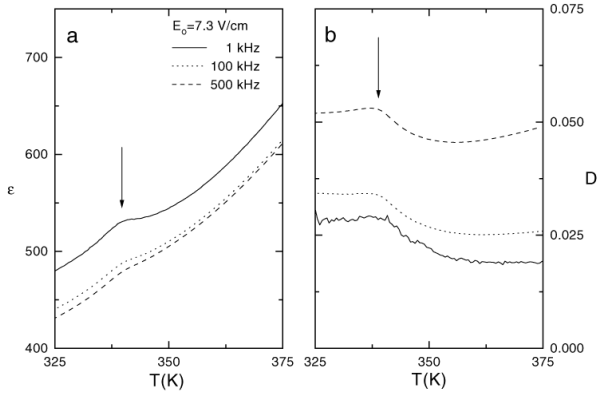


Fig. 4. Dielectric constant and losses factor for one field amplitude and the three frequencies used in the $F_{\rm RL}$-$F_{\rm RH}$ transition.

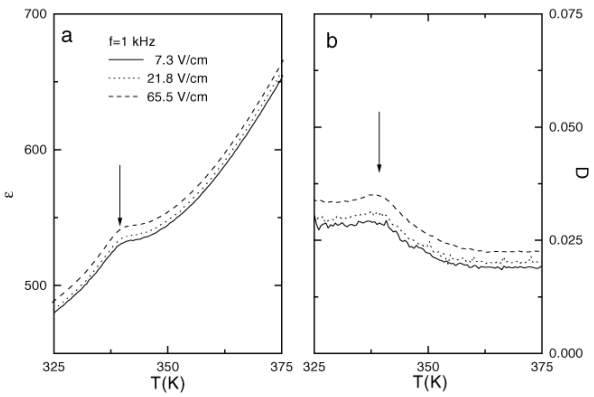


Fig. 5. Dielectric constant and losses in the $F_{RL}$-$F_{RH}$ phase transition for three different fields and the lowest frequency used.

$$\epsilon''(\omega) = \frac{(\epsilon_{ws} - \epsilon_{wo})\omega\tau_w}{1 + \omega^2 2\tau_w^2} \tag{4}$$

where $\epsilon_{ws}(T)$ and $\tau_w(T)$ are strongly temperature dependent at temperatures close to the transition temperature.

At higher frequencies (in the range 500 kHz-2.5 MHz) piezoelectric resonances take place. The pronounced effect of the lowest frequency piezoelectric resonance is observed at the highest frequency used (500 kHz). The dielectric losses peak (see Fig. 1(b)) reveals the importance of the energy dissipation near the resonance frequency in comparison with the other two lower frequencies examined.

For disk geometry, the thickness and the radial vibrational modes are observed. These appear in our samples at different frequencies ($\sim$ 500 kHz in the radial mode, and $\sim$ 2 MHz in the thickness mode at room temperature). Figure 2 represents the dielectric constant ($\epsilon'$ real and $\epsilon''$ imaginary parts) measured at room temperature as a function of frequency in the radial piezoelectric resonance. In this figure, experimental points for $\epsilon'$ , $\epsilon''$ and theoretical fit (solid lines) are presented. The solid lines represents the fit to the resonant behavior, made by

$$\epsilon'(\omega) = \epsilon'_{bg} + A\frac{\omega_o^2 - \omega^2}{(\omega_o^2 - \omega^2)^2 + \omega^2\gamma^2} \tag{5}$$

$$\epsilon''(\omega) = \epsilon''_{bg} + A\frac{\omega^2\gamma^2}{(\omega_o^2 - \omega^2)^2 + \omega^2\gamma^2} \tag{6}$$

where the fit parameters used are $\epsilon'_{bg} \cong 234$, $\epsilon''_{bg} \cong 9$, $A = 2.15$ (rad/s)$^2$, $f_o$=2084 kHz ($\omega_o = 2\pi f_o$), and $\gamma = 1.21\times10^4$ (rad/s). Here, $\epsilon'_{bg}$ and $\epsilon''_{bg}$ are the values of the real and the imaginary part of the dielectric constant far and above from the resonances, and far from strong relaxation regimes. The amplitude $A$ may be expected to be dependent on the reduced mass of ions participating in the vibration, the charge carried by the ions and the density of participating ions per unit volume. The damping parameter, $\gamma$, is expected to depend on the piezoelectric coefficient $d$ as $\gamma \propto 1/d$, known to behave as $d \cong d_o + B/(T - T_o)$ near the transition temperature. The characteristic frequency, $\omega_o$, apparently depends weakly on the temperature.

In dielectrics with permanent and reorientable dipoles, the dielectric constant depends on frequency following Debye's equations [6] for a given temperature:

$$\epsilon'(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2} \tag{7}$$

$$\epsilon''(\omega) = \frac{(\epsilon_s - \epsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \tag{8}$$

where $\epsilon_s$ and $\epsilon_\infty$ are the static and the high frequency dielectric constant, respectively, and $\tau$ is the intrinsic relaxation time. Here $\epsilon_s(T)$ and $\tau(T)$ are strongly dependent with temperature in the vicinity of the transition temperature. It has been found that the intrinsic relaxation of the orientational polarization at room temperature takes place around $10^{10}$ Hz for Zr rich PZT [7].

Figure 3 shows the inverse of the dielectric constant and the losses factor *vs.* temperature for the lowest frequency (1 kHz) at the three fields used in this work. In Fig. 3(a) a small shift in $\epsilon^{-1}$ with the amplitude of the applied field is observed below the $F_{RH}$-$P_C$ transition temperature. At $T > T_{FP}$ the dielectric constant does not depends on field, for those used here, because the spontaneous polarization is zero ($P_s = 0$) above the transition. The temperature dependence of losses factor $D$ at 1 kHz for these amplitudes is given. Dielectric losses present a maximum close to a transition temperature which is shifted in temperature by increasing the applied field, as noted in the literature [5]. We did not get appreciable temperature shifts of the losses maximum for this phase transition for the applied fields, however the height of this peaks increases with increasing the a.c. field amplitude. It is observed that for $T < T_{FP}$ , this effect clearly disappears at temperatures above $T_{FP}$, at which the material is in the non-polar phase.

The results obtained for $\epsilon(T)$ and $D(T)$ at the $F_{RL}$-$F_{RH}$ phase transition are plotted in Figs. 4 (three frequencies at $E_o$=7.3 V/cm) and 5 (three fields at f=1 kHz). Arrows indicate the position of $F_{RL}$-$F_{RH}$ transition temperature. Figure 4(a) shows the dielectric constant for 7.3 V/cm field amplitude at different frequencies. When the frequency is increased, the $F_{RL}$-$F_{RH}$ phase transition becomes more diffuse. In Fig. 4(b) the same phase transition is well defined by the maximum in the losses factor. In this phase transition, cations further displacements and oxygen octahedra rotations takes place [8] along and about the [111] crystallographic direction, respectively. The ionic movements are somewhat sensitive to low frequency fields. The masses of the participating ions are very large in comparison with the

electron mass. The anomalies in dielectric constant become weaker when the frequency of the applied electric field is increased.

In Fig. 5 the $F_{RL}$-$F_{RH}$ phase transition is also shown, for 1 kHz, at the three applied fields. With increasing field amplitude, both $\epsilon$ and D are slightly increased. This transition becomes also better definited with ncreasing field amplitude. No shift in temperature of maximum losses is observed as was the case in the $F_{RH}$-$P_C$ phase transition.

In summary, the factors to be taken into account to analyze the frequency dependence are: the ionic conductivity ($\sim$ 1 kHz), domain wall relaxation (estimated to be about 20 to 500 kHz), not observed in any detail here, the piezoelectric resonances (100 kHz to 2 MHz) and the intrinsic relaxation ($\sim$ 200 MHz). The last three present a pronouncred temperature dependence near the ferroelectric-paraelectric transition temperature. The losses factor peak at $T \sim T_{LH}$ and $T \sim T_{FP}$ increases significantly for larger field amplitudes.

## ACKNOWLEDGMENTS

We acknowledge the support of CICyT (Grant No PB96-0037) and NATO (Grant No CGR-0037).

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